

Promising ferrimagnetic double perovskite oxides towards high spin polarization at high temperature

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We predict through our first-principles calculations that four double perovskite oxides of Bi_2ABO_6 (AB = FeMo, MnMo, MnOs, CrOs) are half-metallic ferrimagnets. Our calculated results shows that the four optimized structures have negative formation energy, from -0.42 to -0.26 eV per formula unit, which implies that they could probably be realized. In the case of $\text{Bi}_2\text{FeMoO}_6$, the half-metallic gap and Curie temperature are predicted to reach to 0.71 eV and 650 K, respectively, which indicates that high spin polarization could be kept at high temperatures far beyond room temperature. It is believed that some of them could be synthesized soon and would prove useful for spintronic applications.

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I. INTRODUCTION

Magnetic materials that have high spin polarization at room temperature or higher are highly desirable for spintronic applications^{1,2}. Half-metallic materials are good candidates because they can have high spin polarization at high temperature³. In the case of CrO_2 , 96% spin polarization has been achieved experimentally². Since 1998, double perovskite oxides have been explored extensively for this purpose because both half-metallicity and high Curie temperature can be achieved in such materials^{4,5}. It has been shown experimentally that several double perovskite oxides, such as $\text{Sr}_2\text{FeMoO}_6$ and $\text{Sr}_2\text{CrReO}_6$ materials⁵, can keep their ferromagnetic or ferrimagnetic phases far beyond room temperature, and more importantly, high-quality materials have been realized recently⁶⁻¹¹.

Here, we present our first-principles exploration on double perovskite oxides of Bi_2ABO_6 with A being 3d transition metals and B 4d/5d ones. We optimize their structures fully and then investigate their stability, electronic structures, and magnetic properties. We find four half-metallic ferrimagnetic materials with negative formation energies. For the best case of $\text{Bi}_2\text{FeMoO}_6$, the half-metallic gap and Curie temperature reach to 0.71 eV and 650 K, respectively. This means that high spin polarization could be realized at high temperatures well above room temperature. More detailed results will be presented in the following.

II. COMPUTATIONAL DETAILS

We use the pseudo-potential and plane wave methods within the density functional theory (DFT)¹², as imple-

mented in package VASP¹³. We use generalized gradient approximation (GGA)¹⁴ for the exchange-correlation potential. In addition to usual valence states, the semicore d states are considered for Bi and the semicore p states for Cr, Mn, Fe, Mo, and Os. Scalar approximation is used for relativistic effect¹⁵, and the spin-orbit coupling is neglected because it has little effect on our main conclusion (to be detailed in the following). We use Monkhorst-Pack method to generates the K-point mesh¹⁶, choosing $6 \times 6 \times 6$ ($6 \times 6 \times 4$) for structure optimizations and total energy calculations of 10-atom (20-atom) unit cells and $12 \times 12 \times 12$ for electronic structure calculations. The cut-off energy is set to 500 eV and the criteria for convergence is 10^{-6} eV for electronic steps and 0.005 eV/Å on atoms for ionic steps.

Metropolis algorithm and variants are used for our Monte Carlo simulations^{17,18}. Phase transition temperatures T_c are determined through investigating the average magnetization, magnetic susceptibility, and fourth-order Binder's cumulant as functions of temperature¹⁸. Several three-dimensional lattices of upto $30 \times 30 \times 30$ magnetic unit cells with periodic boundary condition are used in these calculations. The first 90,000 Monte Carlo steps (MCS) of total 150,000 MCS are used for the thermal equilibrium, and the remaining 60,000 MCS are used to calculate the average magnetization for a given temperature. The Curie temperature T_c value is determined through investigating the magnetization as a function of temperature.

III. MAIN CALCULATED RESULTS AND ANALYSIS

Comparing $\text{Sr}_2\text{FeMoO}_6$ ⁵, $\text{Bi}_2\text{FeCrO}_6$ ^{6,7,19,20} and others similar⁸⁻¹¹, we consider double perovskite structure of formula Bi_2ABO_6 , taking some 3d transition-metal elements for A and some 4d/5d for B. We optimize fully their crystal structures in terms of the unit cell

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of the 10 atoms. The optimized Bi_2ABO_6 has space group Rc (#146). This crystal structure, similar to R3c (#161), is distorted from cubic double perovskite structure, has rhombohedral symmetry, and includes 10 internal parameters^{5,10,11}. We shall present four of the Bi_2ABO_6 compounds, for AB = FeMo, MnMo, MnOs, and CrOs, because they have negative formation energies so that their experimental realization should be probable. Our optimized structural parameters of the four Bi_2ABO_6 compounds are summarized in Table I. The total magnetic moments per formula unit and the partial moments in the spheres of the magnetic A and B atoms are summarized in Table II. The magnetic moments in the spheres of other atoms are much smaller. The total moments are integers in unit of Bohr magneton μ_B , showing a feature of half-metallicity³. The magnetic moment at the A atom is antiparallel to that at the B atom, which means that the magnetic order in these compounds is ferrimagnetic.

TABLE I. Optimized structural parameters of double perovskite Bi_2ABO_6 with the Rc (#146) crystal structure for AB = FeMo, MnMo, MnOs, and CrOs.

AB	FeMo	MnMo	MnOs	CrOs
a (Å)	5.725	5.779	5.761	5.771
c (Å)	14.054	14.093	13.607	12.816
α (°)	59.91	60.20	61.61	64.37
Bi z_1	0.9881	0.9859	0.9917	0.0294
Bi z'_1	0.4837	0.4851	0.4923	0.5071
A z_2	0.2589	0.2572	0.2593	0.2682
B z'_2	0.7675	0.7657	0.7647	0.2681
O x_3	0.5504	0.5612	0.5534	0.4811
O x'_3	0.0506	0.0471	0.0520	0.0558
O y_3	0.9357	0.9220	0.9273	0.9353
O y'_3	0.4350	0.4397	0.4348	0.4287
O z_3	0.1022	0.1036	0.0981	0.1075
O z'_3	0.6099	0.6145	0.6085	0.6009

In Fig. 1 we present spin-resolved density of states (DOS, in states/eV per formula unit) between -7.7 and 3 eV of the double perovskite $\text{Bi}_2\text{FeMoO}_6$ and $\text{Bi}_2\text{MnMoO}_6$. The total DOS in majority-spin channel is zero at the Fermi level in both of the cases. This indicates that the two double perovskite compounds are half-metallic, in agreement with the integral magnetic moments in unit of μ_B . In Fig. 2 we present spin-resolved density of states between -8 and 3 eV of the double perovskite $\text{Bi}_2\text{MnOsO}_6$ and $\text{Bi}_2\text{CrOsO}_6$. They are both half-metallic, too, but it is in minority-spin channel that the total DOS at the Fermi level is equivalent to zero in these two cases. The filled electronic states near the Fermi level originate mainly from the B atom (Mo or Os). We can use half-metallic gap E_g as the key parameter to describe the half-metallic property^{3,21–23}. The E_g values of the four compounds, from 0.25 to 0.71 eV, are summarized in Table II. For the $\text{Bi}_2\text{FeMoO}_6$, E_g is equivalent to 0.71 eV, which implies that high spin polarization could be robust even after the spin-orbit coupling is taken into

account.

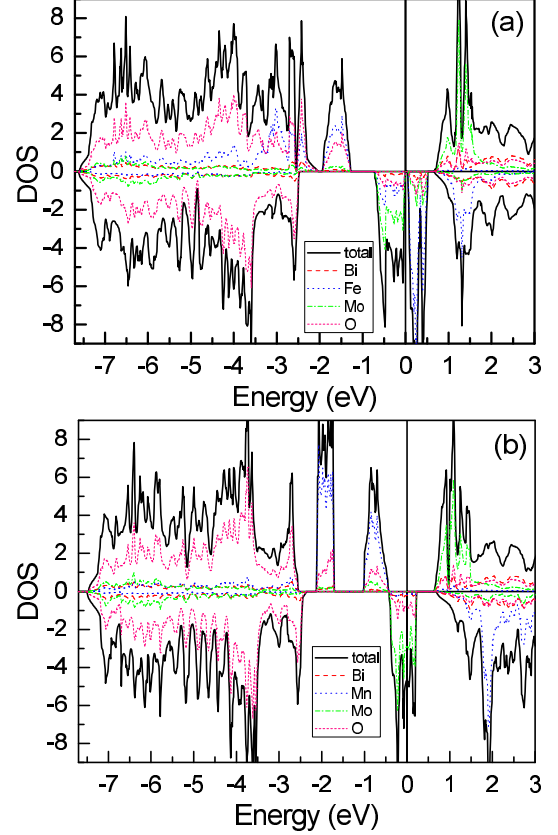


FIG. 1. (color online) Spin-resolved density of states (DOS, in state/eV per formula unit) of double perovskite Bi_2ABO_6 for AB=FeMo (a) and AB=MnMo (b). The solid line is total DOS, and short-dashed, dot-dashed, and dotted lines refer to partial DOS projected in the atomic spheres of Bi, A, B, and O, respectively. The upper part in each panel is majority-spin DOS result, and the lower the minority-spin one.

We investigate their formation energies to determine the stability of these materials towards experimental realization. For achieving reasonable reliability, we choose stable and reachable compounds as our references, and try to use those reference compounds whose valence states concerned are close to those of our compounds. Therefore, we use Bi_2O_3 , Cr_3O_4 , Mn_3O_4 , Fe_3O_4 , MoO_2 , and OsO_2 for our reference compounds for calculating the formation energies. The formation energy is defined as

$$E_f = E(\text{Bi}_2\text{ABO}_6) - E_{\text{ref}}, \quad (1)$$

where $E(X)$ is the total energy of X, and E_{ref} is defined as $E(\text{Bi}_2\text{O}_3) + \frac{1}{3}E(\text{A}_3\text{O}_4) + 2E(\text{BO}_2) - \frac{7}{6}E(\text{O}_2)$. This criteria is much more severe than merely using AO compound or bulk A materials because O atom in the gas state has higher energy than in compounds such as Fe_3O_4 . This should be more precise because the bonds in our materials are almost formed between metal atom and O, not between metal atoms. The formation energies for the

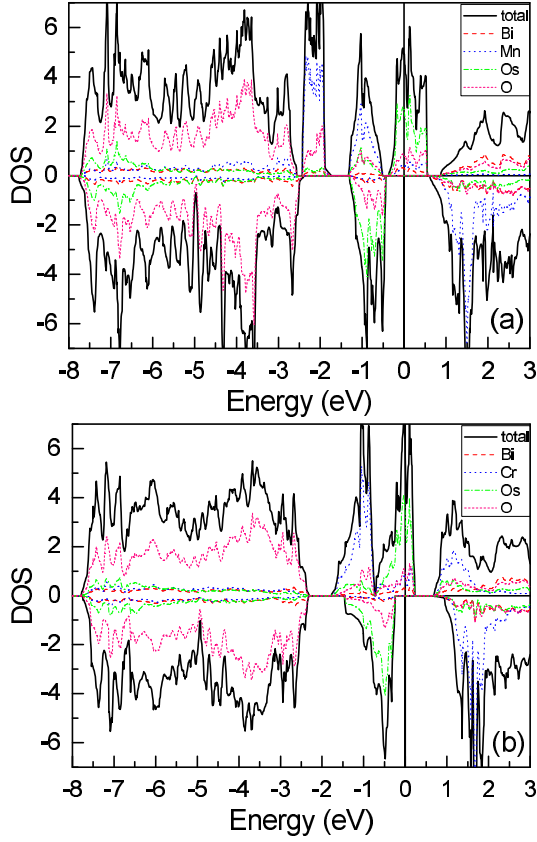


FIG. 2. (color online) Spin-resolved density of states (DOS, in state/eV per formula unit) of double perovskite Bi_2ABO_6 for $\text{AB}=\text{MnOs}$ (a) and $\text{AB}=\text{CrOs}$ (b). The solid line is total DOS, and short-dashed, dot-dashed, and dotted lines refer to partial DOS projected in the atomic spheres of Bi, A, B, and O, respectively. The upper part in each panel is majority-spin DOS result, and the lower the minority-spin one.

four compounds are summarized in Table II. The negative values means that they should probably be realized.

TABLE II. Calculated values of formation energy (E_f in eV), magnetic moment of atom A (M_A in μ_B), magnetic moment of atom B (M_B in μ_B), total magnetic moment (M in μ_B per formula unit), half-metallic gap (E_g in eV), and Curie temperature (T_c in K) of double perovskite Bi_2ABO_6 for $\text{AB} = \text{FeMo}$, MnMo , MnOs , and CrOs .

AB	FeMo	MnMo	MnOs	CrOs
M_A	3.638	4.279	4.066	2.636
M_B	-1.755	-1.391	-1.041	-0.613
M	2.000	3.000	3.000	2.000
E_g	0.71	0.47	0.46	0.25
E_f	-0.41	-0.26	-0.42	-0.29
T_c	650	255	174	201

In order to estimate the Curie temperatures (T_c) of the materials, we calculate the spin exchange interactions between the nearest and next nearest neighboring magnetic atoms (A and B) in terms of the 20-atom unit

cells. Rigorously speaking, there are some induced spin density in the spheres of the Bi and O atoms, less than $0.05\mu_B$. Because they are very small compared to those in the spheres of the magnetic atoms, we shall consider only the magnetic atoms in the following. Actually, A and B atoms form a lattice of magnetic unit cells (cubic unit cells of a NaCl crystal structure)^{5,10,11}. In these calculations, we fix the structures and change the magnetic orders of A and B atoms. In order to make the electronic steps converge for a magnetic order, the linear mixing parameter should be decreased to a small value, 0.1 or smaller. Through comparing the total energies, we obtain the spin exchange interaction constants: J_{AB} for the nearest A and B pair, J_{AA} and J_{BB} for the A-A and B-B next nearest pairs. J_{AB} is dominant over the others. The resultant spin Hamiltonian reads:

$$H = \sum_{\langle ij \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j \quad (2)$$

where \vec{S}_i is spin operator at site i (in both of the A and B sublattices), the summation is over spin pairs, and the spin interaction constant J_{ij} is limited to the nearest and the next nearest neighboring spins.

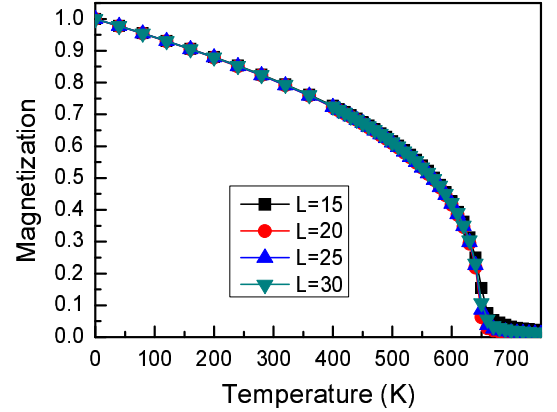


FIG. 3. (color online) Average normalized magnetizations as functions of temperature for double perovskite $\text{Bi}_2\text{FeMoO}_6$ for four different L values. Monte Carlo simulations are done with $L \times L \times L$ magnetic unit cells.

We carry out Monte Carlo simulations to estimate the T_c of the materials^{17,18}. It is well known that Curie temperature will be a little underestimated if classical approximation to the Heisenberg model (2) is used in the Monte Carlo simulation, but it must be much overestimated if the model (2) is reduced to Ising model. For comparison, we do our Monte carlo simulations with both of the approximate models. We present the average normalized magnetization of $\text{Bi}_2\text{FeMoO}_6$, from classical Heisenberg model, as a representative in Fig. 3. The T_c value can be estimated to be 650 K. The others can be done in the same way. The calculated T_c values are summarized in Table II. In contrast, the Ising model results are 1010, 396, 264, and 270 K for $\text{AB} =$

FeMo, MnMo, MnOs, and CrOs, respectively. Therefore, the Curie temperatures for the four half-metallic ferrimagnets are, at least, 650, 255, 174, and 201 K for $\text{Bi}_2\text{FeMoO}_6$, $\text{Bi}_2\text{MnMoO}_6$, $\text{Bi}_2\text{MnOsO}_6$, and $\text{Bi}_2\text{CrOsO}_6$, respectively. High Curie temperature well above room temperature could be realized in $\text{Bi}_2\text{FeMoO}_6$.

IV. DISCUSSIONS AND CONCLUSION

Our calculated results shows that the spin exchange interaction between the nearest A and B atoms is positive, and the A-A and B-B interactions are either weak or negative depending on specific A and B atoms^{10,11}. In the case of $\text{Bi}_2\text{FeMoO}_6$, our calculations show that the nearest A-B spin exchange energy is 39.2 meV, and the nearest A-A and B-B spin exchange energies are 0.13 and -0.71 meV, respectively. The main spin interaction is intermediated by the O atom in between the magnetic A and B atoms, with the A-O-B bond angle being almost 180° , and therefore, it is an antiferromagnetic superexchange. The A atom contributes a different magnetic moment from the B atom so that ferrimagnetism is formed in these double perovskite compounds. Possible overlapping of the nearest O wave functions should play some roles in these compounds, but the main mechanism for the ferrimagnetism must be the antiferromagnetic superexchange between the nearest A and B atoms.

In summary, our first-principles calculations show that four double perovskite oxides, Bi_2ABO_6 ($\text{AB} = \text{FeMo}, \text{MnMo}, \text{MnOs}, \text{and CrOs}$), have negative formation energy, from -0.42 to -0.26 eV per formula unit. In the case of $\text{Bi}_2\text{FeMoO}_6$, our calculated results uncover that its half-metallic gap and Curie temperature reach to 0.71 eV and 650 K, respectively. These indicates that they could probably be realized and high spin polarization could be achieved at high temperature. We believe that at least some of them could be synthesized soon and would prove useful for spintronic applications.

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